Rational using of natural sorbents to receive the clean drinking water

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Abstract

Here is a results of research of the catalytic properties of activated adsorption of natural sorbents - bentonite clays in relation to the most common pesticides: DDT - 8, DDD - 10, DDE - 8,1, γ - HCH - 10, α - HCH - 10, β - HCH - 10, TMTD – 10, karbofos – 10.

Аннотация

Приведены результаты исследования процесса адсорбции и каталитических свойств активированных природных сорбентов - бентонитовых глин различной модификации для наиболее распространенных пестицидов: ДДТ, ДДД, ДДЕ, α,-β,-γ-ТХЦГ, ТМТД, а также карбофоса.

Keywords: drinking water, natural sorbents, bentonite clays, ozonation , catalytic

Introduction

The sharp deterioration of the main sources of water supply, which was formed as a result of poor economic activity, water pollution and groundwater aquifers by nitrates, pesticides, phosphates, phenols, heavy metals, petroleum products, pesticides, radionuclides and pathogens, led to breach the natural processes of self-purification of water bodies and sharpened the problem to get the clean drinking water to the existing water supply stations. For the city of Cherkasy the main supplier of drinking water is water treatment plant of water preparation, which is located at 500 m below the village of Sokurne on the bank of the Dnieper.

The chemical composition of water in the reservoir is determined mainly by the entry of toxic connections from the upper and middle flows of the Dnieper. Mostly water has no odor (1–2 points); transparency varies from 25 -30 cm; chromaticity changes from 30 to 60 degrees. By its composition water belongs to the hydro-carbonate-calcium type. Dissolved oxygen content ranges from 7.29 to 11.9 mg/L, BOD_5 - within acceptable limits, but sometimes reaches 7.52 mg/L. Active reaction of the environment (pH) mainly is neutral (7.0 -7.9) and weakly alkaline (8.0 - 8.7).

The statistical analysis of water pollution of the river of Dnieper showed that the average indicators by the contents of ammonium ions, nitrates, nitrites and heavy metal ions (iron, manganese, copper, zinc, molybdenum, arsenic, lead, chromium and nickel) in the last decade increased by 2-20 times; in the natural water was found the organic impurities, humic acid and fulvic acids (respectively 254-420 and 18000-26000 mg/L). Besides the organic compounds of natural origin there was recorded the aliphatic hydrocarbons C_6H_{14} – $C_{10}H_{22}$, aromatic hydrocarbons (benzene, toluene, ethyl alcohol), acetaldehyde, diethyl ether, tetrahydrofuran and others in the water that has the anthropogenic origin. The content of each measured in tens or hundreds of mkg/l which considerably exceeds the maximum permissible concentration (MPC) based on the international standards for drinking water.

Methods

During chlorination of such solution the number of low molecular organic compounds is increased by 2-3 times; synthesized the isomers of saturated hydrocarbons, simple alcohols, esters, vinyl acetate, propilatsetat; tetrahydrofuran, ethylbenzene, ortoparaksynoly, metoparaksynoly and paraxylene, diethyl ether and chlorine derivatives. The required dose of ozone increases from 2 to 6,4-8,5 g/m^3 which completely eliminates the possibility of using of ozone in the stage of water treatment from an economic standpoint.

To reduce the content of organic connections in the water before chlorination stage is proposed to use the natural sorbents. As a raw material for the production of natural sorbents should be used the bentonite clay of Cherkassy field, which developed by Dashukivski industrial complex, with a total of all layers of more than 50 million tons.

Research that were conducted at the laboratory of environmental problems of Cherkassy State Technological University allow stating that adsorption ability of bentonite clay of different levels (relative to organic compounds) can be higher when they pass different stages of activation. Reference designation numbers of activated clay connected with its geological origin, that points to the placement its layer in the geological composition of bentonite thickness. The main methods of activation of clay were used:

1. An alkaline activation method (the modified clay of the corresponding layer which obtained by the processing of salt additives at medium temperatures) 2Щ-400 means the alkaline processing of clay of second level at the temperature 400^oC.

2. Acid activation method (clay of the corresponding layer received by processing of acidic solutions at certain temperatures). 2K-100 means the acid activated of clay of second level at the temperature 100^oC.

3. The method of medium-temperature processing - 4T-400 - means the granulation processing of natural clay of the fourth level at the temperature 400^oC without modified additives.

These types of activated clays were compared by their adsorption properties with natural clay, which was granulation (for example 2B, 3B and 4B) at the temperature 100-150 ^oC.

1. Results and Discussion

Were conducted the laboratory studies for water purification from different connections. Was established that modification of 2K-100 (the clay of the second level processed with acid solutions at certain temperatures) and 4Щ-400 (the clay of the fourth level processed with salt additives at medium temperatures) has adsorption capacitance which is higher in 3-10 times for a number of toxic connections. The goal of this work is to determine the adsorption capacitance for such connections as pesticides, namely: DDT and its metabolites, DDD and DDYE, α-, β-, γ- HCH, TMTD and karbofos. These compounds are often used in the household of Ukraine. They are toxic and harmful for the health of humans and animals. The massive using of DDT in the past has prompted contamination of underground water, air, surface water bodies (the period of decay of DDT in the air is about 40 years). Besides, these pesticides have properties to accumulate in the fatty tissues of the human body, which leads to negative consequences.

To obtain the necessary data in the stages of adsorption of pesticides conducted the research to reduce the content of organic compounds.

Adsorption researches were conducted on the column which was filled with granulated clay with size of granule is 1- 2.5 mm, and - 5 mm. To provide the sturdiness the granules baked in a muffle furnace. Clay after preparation(one by one every faction) covered the column by layers: 10 g of clay with mass of 10-25 g and size 1-2.5 mm. The total mass of sorbent in the adsorption column was 35 g and the height of a layer of sorbent was 100 mm. After that through the layer of sorbent passed water (100 ml) by fractional method which was known the number of pesticides. The rate of expiration of water was 10 drops per second. o prevent water washed the smallest particles of clay from the column the bottom of the column put a metal grid and a layer of glass wool over it. The content of pesticides was determined in each 100 ml of purified water.

As the solvent during analyzes on pesticides were selected n-hexane. For analysis used the solvent of brands of C.C. To preparation of the aqueous solutions was used the bidistillate. Under the task to prepare the water meant to add on it a certain amount of each pesticide in the amount which would not exceeding 10 MAC. For this were took the standard which is an ampoule where as a powder or organic solution is given pesticide. Prepared the standard solution where was n-hexane as the solvent. The concentration of the standard solution was 0.1 mg/ml. Therefore, the water solutions were prepared close to 10 MAC: 1ml of primary standard solution was added to 100 ml of water. The concentration of pesticides in samples water solutions was (in MAC): DDT - 8, DDD - 10, DDE -8,1, γ - HCH - 10, α - HCH - 10 , β - HCH - 10, karbofos – 10, TMTD - 10.

Before we pass the water through the column with a sorbent we determined the concentration of pesticides in water. After two hours of shaking the solution the number of pesticides which has moved into the water was determined by an additional analysis. This analysis consists of evaporation of dryness, add 2 - 3 ml of n-hexane and then determine the amount of pesticides by gas-liquid chromatography. The results of this analysis are included in the table 1.

Table 1 Number of pesticides in the water after saturation

Name of the pesticide	Number of pesticides in the working solution,% of introduced
DDT	**80**
DDD	**97**
DDE	**100**
α - HCH	**100**
β - HCH	**100**
γ - HCH	**100**
TMTD	**50**
Karbofos	**100**

After determining the initial concentration of pesticides in the water solution, it’s sent to the stage of adsorption cleaning by natural sorbent.

The best results from the equilibrium adsorption capacities for all pesticides gave the clay of brand 4T-100 with the symbol 2.

From results of the analysis we can conclude that, the bentonite clay has the property to effectively absorbing from the water some dissolved organic compounds, in particular, pesticides.

Determination of the dynamic volumetric capacity of the activated clays in relation to pesticides was performed by the adsorption column with fixed bed of sorbent by the previously presented method. The rate of water filtration determined successively: first, by stream and then by 10 drops/sec.

According to the results of experiments determined that the dynamic volumetric capacity also is higher in clay with the symbol 2. For clay №1 it is 0, 1398 mg/g of clay; for clay №2 - 0, 2019 mg/g of clay. Handling the results of the analysis carried out by the method of least squares. Results of the analysis were obtained with the gas-liquid chromatograph brand "Colour-500" which with the help of computer and device gave results in the form of computer chromatogram. Each peak in the chromatogram goes in its characteristic time. The time of peak α- i β- HCH (these two pesticide come as a single peak) is about 130 sec, γ - HCH -168 sec, DDE - 630 sec, DDD - 1042 sec, DDT - from 1998 to 2000 sec.

The calculation of peak areas was performed using the programs which are embedded in the computer and using formulas.

The bentonite clays showed high adsorption performance by ions of heavy metals and organic compounds, in particular, pesticides (table 2).

Table 2 Changing some parameters of quality the water of Dnieper which passed through adsorber

№ n/n	**Indicators**	**Average rates of water of Dnipro River**	**Number of Dnieper water which passed through the sorbent, m^3**			
			1	2,5	3,4	**4,8**
1	Chromaticity, °	40	5	22	30	**35**
2	Turbidity, mg/L	0,69	0,46	0,54	0,68	**0,74**
3	Alkalinity, mg-eq /L	2,8	1,9	2,0	2,1	**2,5**
4	Hardness, mg-eq/L	3,0	2,7	2,8	2,9	**3,0**
5	Oxidation mg O_2 /L	12,8	2,2	2,8	4,8	**7,09**
6	Fe^{3+}, mkg/L	565	260	320	370	**560**
7	Cu^{2+}, mkg/L	10,4	2,3	2,9	5,6	**10,4**
8	Ca^{2+}, mg-eq/L	2,3	2,4	2,4	1,9	**2,4**
9	Mg^{2+}, mg-eq/L	0,75	0,75	0,65	0,6	**0,75**
10	NH_4^+, mg/L	0,56	0,54	0,56	0,55	**0,56**
11	NO_3^-, mg/L	3,20	1,95	2,65	2,92	**3,20**
12	NO_2^-, mg/L	0,0170	0,00052	0,0010	0,0032	**0,0071**
13	**Total of pesticides, mkg/L**	**124**	**28**	**36**	**49**	**64**

On the basis of experiments it was found the reduction of such parameters: chromaticity 25-10%, oxidation 82,8-17%; content of heavy metals: iron 43,4-23,5%, copper 78,0-2,2%, zinc 52,0-1,6%; nitrates 38,5-22,7, nitrites 58,8-10%, pesticides 96,4-5,0; chlorine derivatives 100-10,1%. Comparing the initial and final values it is traced the decrease of sorption degree after passing through the sorbent, respectively 1.06 and 5, 30 m^3 of Dnieper water (figure 1). Natural sorbents have no influence on other indicators.

The results shows that the activated bentonite clay absorbs the macromolecular organic compounds (such as humic and fulvic acids which reduces the adsorption capacity of the sorbent) with high speed.

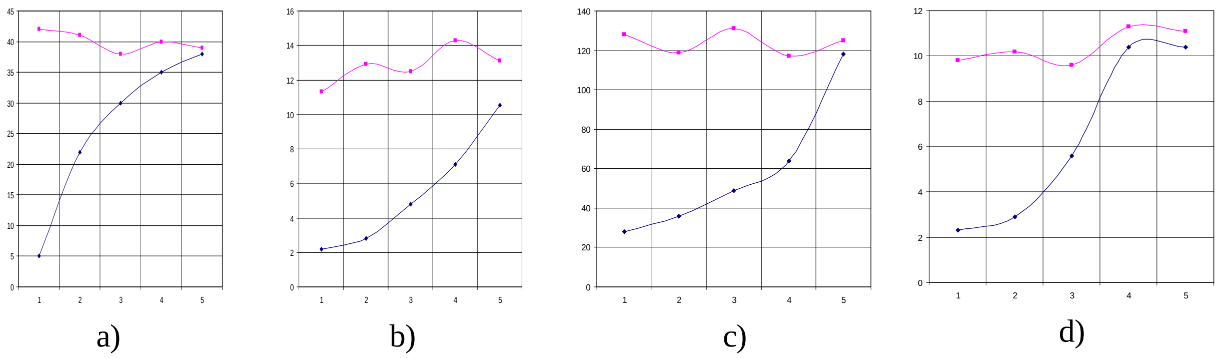


Figure 1 Dependence of changing the indicators of water of Dnieper before and after filtration from the number of transmitted water Q (m^3): a) – chromaticity; b) – oxidation; c) – heavy metals; d) – pesticides.

2. Results and Discussion

Research of catalytic activity of samples of activated bentonite clays of various modifications during ozonolysis of organic compounds in water conducted by comparing the characteristics of the catalytic decomposition on different catalysts. For oxidation of organic contaminants in the summer water of river Dnieper and Ros used such catalytic mass: activated coal and the samples of clays №1, 2, 3 and 4. The primary parameter is the change of degree of water by COD. COD analysis of water held by known methods. As the comparative inactive weight which enabled us to consider the diffusion conditions in the system O_3-O_2-H_2O (COD) been used the glass crumb with size of 2,2 ± 0,1mm in diameter that about to size of the catalytic mass of activated coal and the bentonite clays samples.

To determine the dose of ozone (D_{O_3}) which is used to processing the samples of water constructed the graphical dependencies of ozone concentration inlet and outlet of the ozone generator ($C_{O_3}=f(\tau)$ from the time of water treatment (min) on data obtained in experiments (figures. 2–5).

These doses of ozon orrespond to changing the concentration of COD in the liquid phase.

After scaling of area values were determined the real unit costs of oxidant. The data of D_{O_3} for different initial values of COD is shown in the table 3.

Table 3 The doses of ozone for wastewater treatment with various catalysts

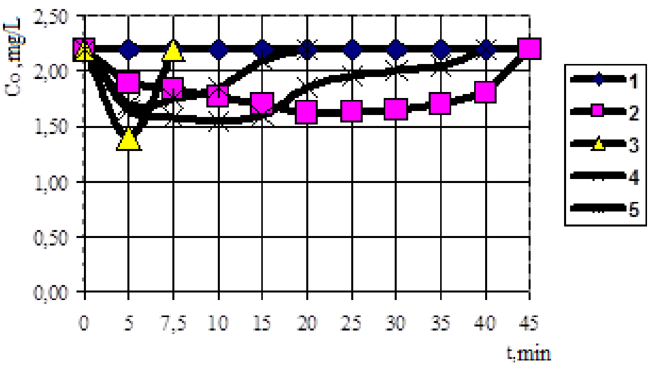
	Catalysts					
	Glass	Coal	Clay №1	Clay №2	Clay №3	**Clay №4**
The time of processing the water τ, min.	40	12	15	15	40	**30**
% of treatment	50	100	91	84	71	**100**
D_{O_3} **, g/L**	**390**	**100**	**340**	**100**	**150**	**282**

Experimental data which are presented in the figures 2-5 suggest that the bentonite clay has the ability to absorb some dissolved organic contaminants rom the waste water and and accelerate the processes of oxidative degradation of organic compounds. Using the bentonite clays as a catalyst during the water ozonation makes it possible to reduce the time of processing and reduce the dose of ozone which should be spend for the full water treatment. Comparing the results of the research, it was determined that the clay №2 the best absorbs some organic impurities from the water. The time of water treatment decreased by 4 times and the cost of ozone - about 5 times.

Established that with increasing the concentration of organic compounds in the water it is necessary to increase the processing time of water. Accordingly the dose of ozon (D_{O_3}) increases approximately in 2,2 times. In this case, the sample of clay №2 also shows an increased activity. The specific dose of oxidant reaches the values which are close to D_{O_3} for activated carbon. The sample of clay №4 makes it possible to reduce the COD almost to zero.

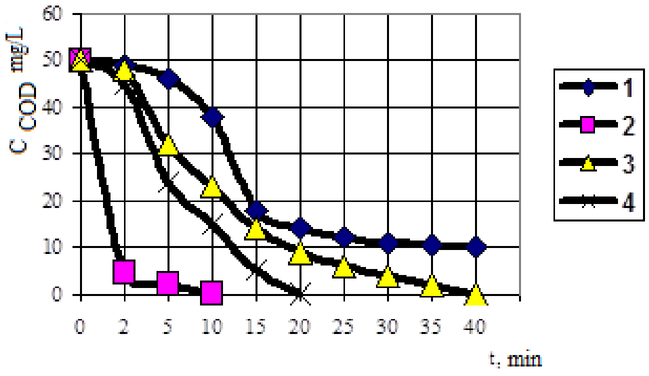
Thus, the clays №2 and №4 have greater catalytic property in the wastewater treatment from organic compounds. The catalytic mass should be composed of two layers of catalysts, the activated bentonite clay of №2 and №4 modifications to achieve the required norms of content of organic compounds.

Low cost of activated bentonite clay and their regeneration allows you to use the proposed catalytic mass to the purification of surface water.



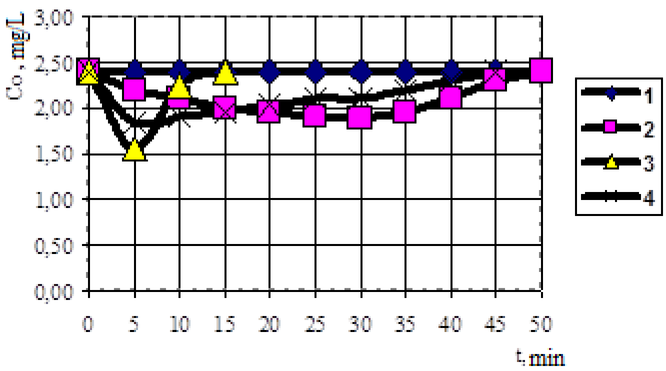
1 - $C^{o}_{O_3}$; 2 - glass; 3 - coal; 4 clay №1; 5 - clay №2.

Figure 2 Dependence the changing of ozone concentration from time before reactor (1) and after reactor (2-4) for various catalytic mass.



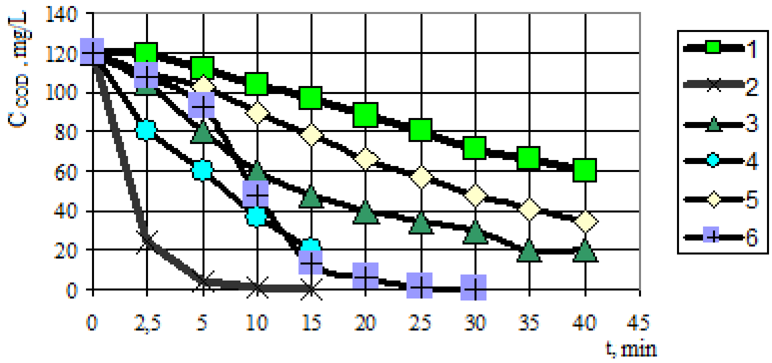
1 - glass; 2 - coal; 3 - 4 clay №1; 4 - 4 clay №2.

Figure 3 Dependence the changing of COD in the liquid phase at different catalytic masses.



1 - $C^o_{O_3}$; 2 - glass; 3 - coal; 4 - clay №3 and №4.

Figure 4 Dependence the changing of ozone concentration from time before reactor (1) and after reactor (2-4) for different catalytic masses.



1 - glass; 2 - coal; 3 - clay №1; 4 - clay №2; 5 - clay №3; 6 – clay №4

Figure 5 Dependence the changing of COD in the liquid phase at different catalytic masses

Conclusions

The activated bentonite clays are the active modified natural sorbents and they can be used both during the adsorption purification of the organic toxic contaminants and at the stage of oxidative chemical degradation of various compounds.

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